USE OF CHEMOMETRICS TO CHARACTERIZE TROPICAL WINES FROM DIFFERENT VINTAGES AND GRAPE CULTIVARS ACCORDING TO THE ^{1}H NMR SPECTROSCOPY DATA

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Summary

Tropical wines have been produced in Northeast of Brazil since 1980's, between the 8° and 9° S latitude, in a region called Sub-middle São Francisco river Valley. This area presents an intra-annual climate variability and wines can be elaborated in different months of the year, according to the winery, with different analytical characteristics due to the climatic conditions. NMR spectroscopy is an interesting tool that allows to determine in a single analysis many analytical compounds of the wines. PCA and PLS multivariate statistical analyses applied on NMR data allow to discriminate samples and to identify the responsible compounds for the clustering. The aim of this work was to use chemometrics, PCA and PLS, applied on ^{1}H NMR spectroscopy data, to characterize tropical wines from different vintages and grape cultivars, in Northeast of Brazil. Wines were elaborated by using traditional winemaking process with control of the fermentations temperature and use of antioxidants. Before statistical analyses, ^{1}H NMR spectra were segmented, normalized, converted to Excel software format and further processed for PCA and PLS analyses. Statistical analyses applied on NMR spectra data were not satisfactory to discriminate between different vintages of white and red wines together, but they were able to separate each one according to different vintages and cultivars. Metabolic compounds were found to explain wine clusters, and fingerprints are discussed.

INTRODUCTION

Traditional winegrowing areas are located in temperate climate conditions, where it is possible to have one harvest per year (Reynier, 2007). Recently, tropical wines have been produced in some countries, as India, Thailand, Venezuela and Brazil. In these conditions, it is possible to have two or three harvests per year, according to the genetic and productive cycle of different cultivars. In Brazil, the main characteristics allowing vines a continuous vegetative development, and then grapevine cropping throughout the year, are an annual average temperature of 26.4 °C (21.0 °C minimum and 31.7 °C maximum), high luminosity (about 3000 hours of luminosity year^{-1}) and water available for irrigation; wines can present different characteristics due to the intra-annual climatic variability (Tonietto and Teixeira, 2004; Teixeira, 2001; Teixeira and Azevedo, 1996).

Proton nuclear magnetic resonance spectroscopy (^{1}H NMR) is a powerful and very useful tool that allows to determine metabolic profiling and/or metabolite fingerprinting of fruits, olive oil, beer, grapes and wines (Pereira *et al.*, 2007; Krishnan *et al.*, 2005; Pereira *et al.*, 2005; Brescia *et al.*, 2002; Fan, 1996). The use of chemometric methods on NMR data, as principal component analysis (PCA) and partial least squares (PLS), allows to separate samples identifying analytical compounds responsible for the clustering (Pereira *et al.*, 2007; Kemsley, 1998). The aim of this paper was to use chemometrics to separate wine samples and to identify analytical markers of tropical wines elaborated in different vintages and grape cultivars in Northeast of Brazil, by means of data obtained by 1D ^{1}H NMR spectroscopy.

MATERIAL AND METHODS

Wines were elaborated in stainless steel tanks of 200 L from seven white and five red grape cultivars harvested in different months between 2005 and 2008. It was used the traditional winemaking process, with control of the fermentations temperature for red (25 °C for alcoholic and 18 °C for malolactic fermentation) and white wines (18 °C for alcoholic fermentation, only) and use of antioxidant to increase wine quality and stability (Peynaud, 1997). After stabilization, wines were bottled and then analyzed by using a Varian 300 MHz NMR spectrometer to determine one dimension ^{1}H NMR spectra of each wine sample analyzed in triplicate. Spectra were acquired according to our previous work and each spectrum was obtained in about 15 minutes (Pereira *et al.*, 2007). The samples were: i) white wines: Schomburger from November 2005 (Sc05); Schomburger from September 2006 (Sc06); Regner from May 2005 (Re05); Viognier from December 2006 (Vi06); Flora from December 2005 (Fl05); Sauvignon blanc from November 2008 (Sb08); and Colombard from December 2005 (Co05); ii) red wines: Alfrocheiro from June 2006 (Al06); Tempranillo from February 2007 (Te07); Trincadeira from February 2007 (Tr07); Periquita from February 2007 (Pe07); and Petit Verdot from July 2007

(PV07). Before statistical analyses, ^{1}H NMR spectra were segmented into 100 spectral domains (variables) of 0.04 ppm between 0.54 and 5.99 ppm, normalized to the total spectral intensity, then converted to Excel software format and further processed with Win-Das software for PCA and PLS analyses.

RESULTS AND DISCUSSION

Statistical analyses obtained of 36 ^{1}H NMR spectra of red and white wine samples from different vintages together were not efficient to discriminate clusters (data not shown). However, multivariate statistical analyses were able to discriminate between wine samples from different grape cultivars. Figure 1 shows PC1 x PC2 plot obtained from 21 ^{1}H NMR spectra of seven white wines analyzed. Wines of the grape cultivar Schombürger elaborated in two vintages (November 2005 and September 2006) presented similarities and are located in the positive side of PC1. Even if climatic conditions were different in the two years, wines were similar, and in this case the most important factor was genetic. The chemical shifts-characterizing these samples were not identified (5.33 and 5.99 ppm), but it can be suggested some aromatic compounds (Fan, 1996). In the positive side of PC2 are located wine samples of Sauvignon blanc (Sb08), characterized by the shifts 3.68 ppm, identified as glycerol, 4.83 ppm (residual water) and 4.06 ppm (unknown). In the negative side of the axes PC1 and PC2 are located the wine samples of Regner (Re06), and chemical shifts responsible for discrimination were 2.69 ppm, identified as pyruvic and succinic acids, 4.56 ppm, identified as tartaric acid, 0.87 ppm (unknown) and 3.51 ppm (glycerol). According to previous works, organic acids and glycerol can be considered as important discriminating factors to separate wines, explained by genetic influence and cultivar adaptation to the edafo-climatic conditions of the region (Silva Neto *et al.*, 2009; Pereira *et al.*, 2007; Reynier, 2007).

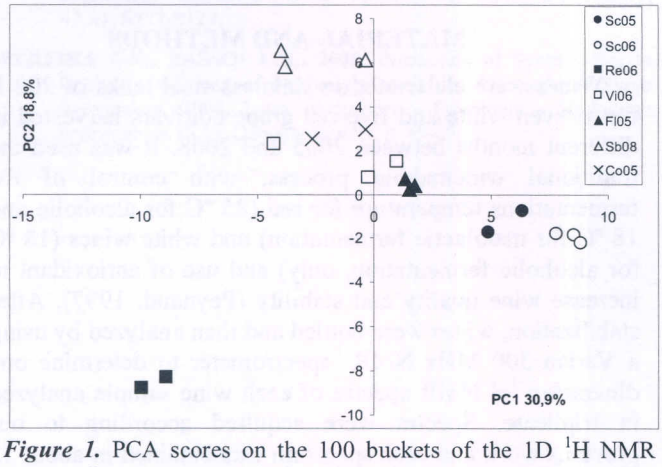

Figure 1. PCA scores on the 100 buckets of the 1D ^{1}H NMR spectra from seven tropical white wines with triplicates. The PC1/PC2 plot explained 49.7% of the total variance, where: Sc05: Schomburger 2005; Sc06: Schomburger 2006; Re06: Regner 2006; Vi06: Viognier 2006; Fl05: Flora 2005; Sb08: Sauvignon blanc 2008; Co05: Colombard 2005.

Red wines elaborated from five grape cultivars were very well discriminated according to the PCA (Figure 2) and PLS (data not shown).

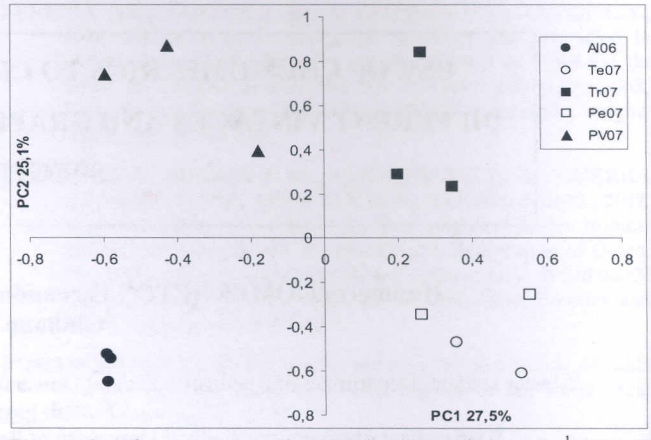

Figure 2. PCA scores on the 100 buckets of the 1D ^{1}H NMR spectra from five tropical red wines with triplicates. The PC1/PC2 plot explained 52.6% of the total variance, where: Al06: Alfrocheiro, 2006; Te07: Tempranillo 2007; Tr07: Trincadeira 2007; Pe07: Periquita 2007; PV07: Petit Verdot 2007.

PC1/PC2 plot explained 52.6% of total variability. In the positive side of PC1 and PC2 are located Trincadeira wines (Tr07) from 2007 vintage. Chemical shifts characterizing these wines were 4.83 ppm (residual water), 4.01 (unknown), 3.68 ppm (glycerol), 4.45 ppm (tartaric acid) and 1.15 ppm (butylenglycol). In the negative side of PC1 and in the positive side of PC2 are Petit Verdot 2007 (PV07) wines, that were characterized by chemical shifts 1.86 and 1.92 ppm (proline). Alfrocheiro wines, located in the negative side of the axes PC1 and PC2, presented, as characteristics, the chemical shifts 4.34 (lactic acid) and 1.86 ppm (unknown). In the positive side of PC1 and in the negative side of PC2 wines from Tempranillo and Periquita, both elaborated in 2007, presented similarities, and chemical shifts were identified as 4.01 (unknown), 3.68 ppm (glycerol) and 1.86 ppm (unknown). For red wines grape cultivar and year of the elaboration had a great importance to discriminate different wines (Silva Neto *et al.*, 2009; Pereira *et al.*, 2007).

CONCLUSIONS

Chemometrics applied on 1D H NMR data allowed to discriminate brazilian tropical wines. The tool was not able to discriminate bewteen red and white wines when analyzed together, presenting some similarities, but when applied to red or white wines separated, it allowed to separate wines according to different climates (month of winemaking) and grape cultivar. The main compounds identified explaining clusterings were glycerol, tartaric, lactic, pyruvic and succinic acids, butylenglycol, proline and some unknown chemical shifts.

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